

# Kinetics of Methanol Oxidation and SEM/EDX analysis of Nanocatalyst Layers after Electrochemical Activation

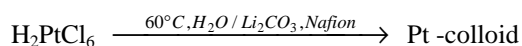
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The aim of this work was the investigation of electrochemical behaviour and the surface of nanocatalyst layers after activation of the catalyst particles.

To prepare the catalyst layers stabilized nanoparticles of Pt resp. Pt/Ru were deposited on different electrode types (RDE,  $\mu$ -electrode, Au foil).

We produced new Pt-nanoparticles in the following way:



So the Pt-colloids with a size of  $\varnothing \sim 2$  nm have Nafion as stabilizer which does not need to be removed before characterization of the catalyst particles. Furthermore the deposition of these colloids on a electrode is successful without fixing the layer with an extra Nafion film.

Composite films of various Pt and Pt/Ru loadings were applied on the electrode.  $i(U)$ -measurements in sulfuric acid with and without methanol were carried out to analyse the kinetics of methanol oxidation for each catalyst layer. We chose this reactant because the activity of methanol oxidation depends on the amount of free Pt surface. So the change of activation of nanoparticles was studied.

Fig. 1 shows the influence of Pt-oxide formation on the nanoparticles on methanol oxidation during potentiodynamic measurements.

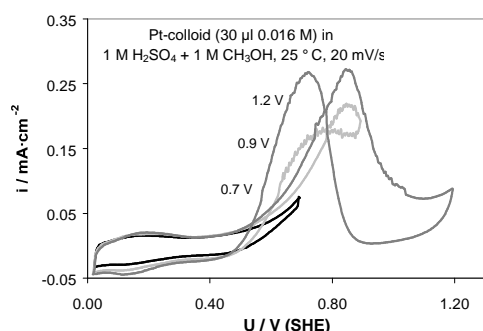


Fig. 1:  $i(U)$ -measurements in 1 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  with variation of reverse potential

At  $U_{\text{reverse}} > 0.80$  V two peaks occur because Pt nanoparticles start to form an oxide film, but  $\text{CH}_3\text{OH}$  molecules can adsorb only at free, i.e. reduced Pt surfaces.

So the retrace shows an increase of current at  $U < 0.85$  V (at  $U_{\text{reverse}} = 1.2$  V) because  $\text{CH}_3\text{OH}$  can adsorb again.

With high  $U_{\text{reverse}}$  the Pt surface gets activated so that the methanol oxidation current rises both in trace and in retrace.

To get better yields of current densities during

potentiostatic pulse measurements we started a small pulse (1s) of 1.1 V to get a Pt oxide layer. A second pulse reduces the Pt oxide and after reduction ( $\log t = -2$ ) methanol oxidation can be observed with higher current densities at  $\log t > -0.75$ , at  $t = 10$  s the current density is doubled (Fig.2). The charge of the Pt oxidation pulse  $q_{\text{ox}}$  is 0.1 mC, the difference of methanol oxidation  $\Delta q_{\text{MeOH}}$  caused by activation is 47 mC. So the loss of charge cause by oxide formation is 2 %.

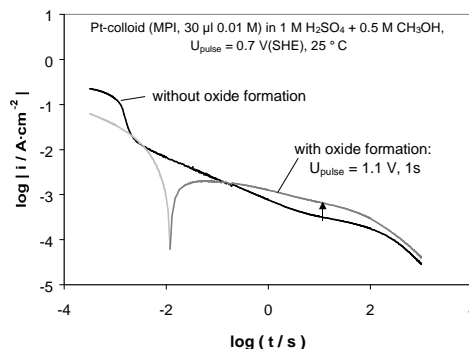


Fig. 2: Current transients with and without oxide formation in 1 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$ , 25 °C

But this electrochemical activation of Pt nanocatalyst layers causes a change in distribution of the elements. Here the EDX mappings of Pt before and after electrochemical treatment are shown. An enrichment of Pt can be observed at the edge of the cracks while the distribution inside the layer does not change.

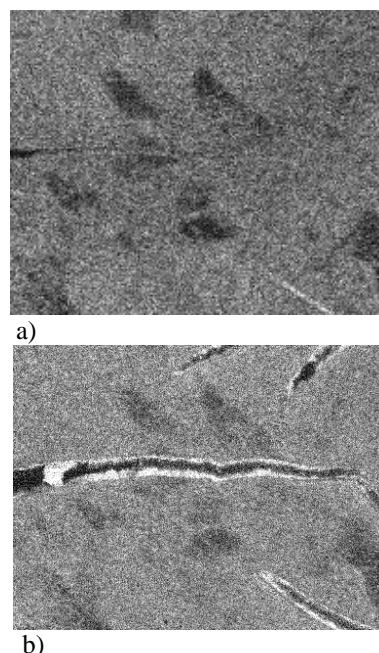


Fig. 3: EDX mappings of Pt a) before and b) after electrochemical treatment

Furthermore  $\mu$ -electrodes were used in studies of fast potentiostatic pulses of  $1\mu\text{s} < t < 100\text{s}$ . So the detection of small charges for  $t < 100$  ms is possible which is impossible at macro electrodes because of ohmic drop in the electrolyte (0.3 mC for  $t < 1\text{s}$ ).

## References:

- [1] T. J. Schmidt, H. A. Gasteiger, G. D. Stäb, P. M. Urban, D. M. Kolb and R. J. Behm; J. Electrochem. Soc. 145 (1998) 2354-2358
- [2] A. Hamnett; in "Interfacial Electrochemistry; Theory, Experiment and Applications", edited by A. Wieckowski; Marcel Dekker, Inc. 1999, 843-883